# High-resolution atomic pair distribution functions of $Ca_{x/2}Al_xSi_{1-x}O_2$ glasses by high-energy x-ray diffraction

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## Introduction

Knowledge of the local atomic ordering in glasses is an important prerequisite to understanding their physical and thermodynamic properties. For calcium aluminosilicate glasses, it is generally accepted that $SiO_4$ and $AlO_4$ tetrahedra are the basic structural units. The tetrahedra are linked together by sharing common oxygen atoms, forming a more or less polymerized network with Ca cations occupying large irregular cavities [1-3]. Oxygens linking two tetrahedral units are called "bridging," while those connecting one tetrahedral cation (Al or Si) with Ca cation are called "non-bridging." Although the non-bridging oxygens (NBOs) are not an integral part of the tetrahedral network, they play an important role in determining the thermodynamic and dynamic properties of silicate glasses [4]. Recent x-ray diffraction studies on the atomic pair distributions in calcium aluminosilicate glasses have suggested that NBOs are located on $SiO_4$ but not $AlO_4$ tetrahedra. However, this outcome is yet to be verified due to the limited real-space resolution of the data [5]. Simple estimates show that Si-O (~1.62 Å) and Al-O (~1.7–1.75 Å) coordination polyhedra may be well differentiated; hence, the distribution of NBOs can be unambiguously explored only when diffraction data extended to wavevectors $Q \sim 50$ Å$^{-1}$ are obtained. Such high wavevectors could be accessed by employing x-rays of high energy (short wavelength) since $Q = 4\pi \sin(\theta)/\lambda$, where $\theta$ is the diffraction (Bragg) angle and $\lambda$ the wavelength of the radiation [6]. The present report describes an experiment aimed at obtaining high real-space resolution structural data for $Ca_{x/2}Al_xSi_{1-x}O_2$ glasses (x=0, 0.25, 0.5) by carrying out high-energy synchrotron radiation experiments.

## Methods and Materials

The diffraction experiment was carried out at the APS bending-magnet beamline 1-BM, operated by SRI-CAT. X-rays of energy 65 keV were used. Three glassy samples with the compositions given above were measured in symmetric transmission geometry at room temperature. A bent, horizontally diffracting Si(111) crystal was used to monochromatize and focus the x-ray beam. Scattered

intensities were collected with an intrinsic Ge solid-state detector coupled to a multichannel analyzer. Due to the limited energy resolution of this experimental setup, it
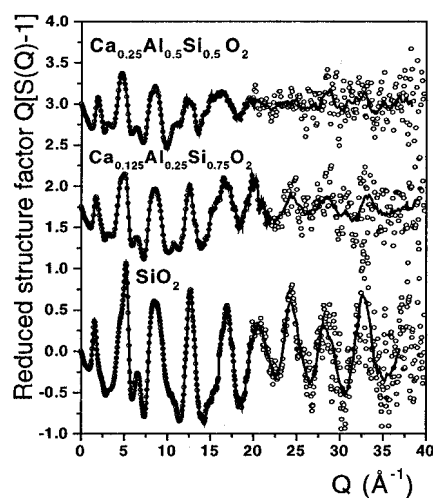


Figure 1: Reduced structure factors for calcium aluminosilicate glasses (circles) together with the optimum smooth line.

was not possible to separate the inelastic (Compton) scattering from the elastic, so both were collected together. This experimental deficiency somewhat complicated the data analysis since, for these glasses, Compton scattering is much stronger than the elastic signal at high values of Q. Several diffraction runs were conducted with each sample and the resulting spectra averaged to improve the statistical accuracy. The intensities collected varied from $5 \times 10^5$ to $5 \times 10^4$ counts at low and high Q, respectively. It took approximately 16 hours per sample to collect them. As can be seen in Fig. 1, this ensured sufficient statistics to Q values as high as 30 Å$^{-1}$ only. The data were normalized for flux, corrected for background scattering, detector dead time, absorption and Compton scattering and then divided by the average form factor to obtain the total structure

factor, S(Q). All data correction procedures were done with the help of the program RAD [7]. Experimental reduced structure factors Q[S(Q)-1] are shown in Fig. 1. Their Fourier associate, the reduced radial distribution functions, G(r), are shown in Fig. 2.
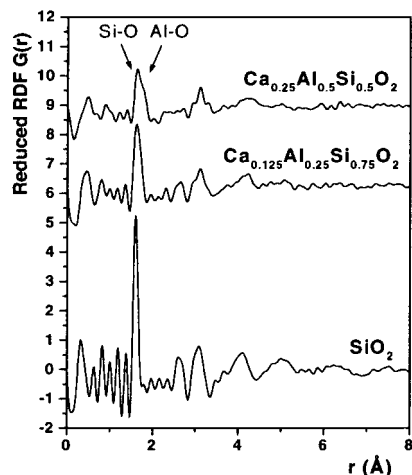


Figure 2: Reduced radial distribution functions for calcium aluminosilicate glasses obtained by Fourier transforming the smoothed data of Fig. 1. First peak in G(r) is almost split up (i.e., Si-O and Al-O polyhedra are on the verge of differentiating in the $Ca_{0.25}Al_{0.5}Si_{0.5}O_2$ glass).

## Results and Discussion

As can be seen in Fig. 1, the experimental structure factors exhibit significant oscillations up until the maximal Q value of approximately 40 $Å^{-1}$ is reached. To better demonstrate this oscillating behaviour, a smooth line is placed through the original data points. An inspection of the smoothed data shows that the amplitude of the oscillations in the structure factors decreases and their positions shift with the increase in Ca/Al content. The changes reflect a gradual change of the glass structure that takes place with the introduction of network-former Al and network-modifier Ca atoms. This change can be quantified by inspecting the corresponding G(r)s shown in Fig. 2. As can be seen in the figure, only the atomic distribution function for silica glass has a sharp first peak. It is positioned at 1.61 ±0.01 Å and reflects the well-defined $SiO_4$ tetrahedral units forming the glass structure. With the increase in Ca and Al content, the height of the peak decreases and its shape becomes asymmetric. It is evidently composed of two components with their magnitude changing with composition. The low-r component may be attributed to Si-O polyhedra and the higher-r component, positioned at approximately 1.75±0.03 Å, to Al-O polyhedral units. Unfortunately, the

resolution of the present data does not allow an unambiguous separation of the two components of the first peak in the experimental G(r)s of the glasses containing Ca and Al. Therefore, Si-O and Al-O first coordination numbers could not be uniquely estimated and the actual distribution of NBOs determined. Diffraction data of better statistical accuracy extended up to at least 50 $Å^{-1}$ are necessary to achieve this goal.

## Conclusion

The present experiment demonstrates that even for weakly scattering materials, like the oxide glasses investigated, structure data extended up to 25-30 $Å^{-1}$ and, if extra smoothing is applied, even up to 40 $Å^{-1}$ may be obtained in cases where a bending magnet (such as at the APS) is employed as a source of radiation. An undulator source to improve the statistical accuracy and a double-crystal monochromator to improve the energy resolution should be employed when data of better statistical accuracy and of higher Q-limit are needed.

## Acknowledgements

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